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Conformational Properties of (*Z*,*Z*)-, (*E*,*Z*)-, and (*E*,*E*)-Cycloocta-1,4-dienes

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Summary. *Ab initio* calculations at the HF/6-31G* level of theory for geometry optimization and the MP2/6-31G*//HF/6-31G* level for a single point total energy calculation are reported for (*Z*,*Z*)-, (*E*,*Z*)-, and (*E*,*E*)-cycloocta-1,4-dienes. The C_2-symmetric twist-boat conformation of (*Z*,*Z*)-cycloocta-1,4-diene was calculated to be by 3.6 kJ · mol^{-1} more stable than the C_S-symmetric boat-chair form; the calculated energy barrier for ring inversion of the twist-boat conformation *via* the C_S-symmetric boat-boat geometry is 19.1 kJ · mol^{-1}. Interconversion between twist-boat and boat-chair conformations takes place *via* a half-chair (C_1) transition state which is 43.5 kJ · mol^{-1} above the twist-boat form. The unsymmetrical twist-boat-chair conformation of (*E*,*Z*)-cycloocta-1,4-diene was calculated to be by 18.7 kJ · mol^{-1} more stable than the unsymmetrical boat-chair form. The calculated energy barrier for the interconversion of twist-boat-chair and boat-chair is 69.5 kJ · mol^{-1}, whereas the barrier for swiveling of the *trans*-double bond through the bridge is 172.6 kJ · mol^{-1}. The C_S symmetric crown conformation of the parallel family of (*E*,*E*)-cycloocta-1,4-diene was calculated to be by 16.5 kJ · mol^{-1} more stable than the C_S-symmetric boat-chair form. Interconversion of crown and boat-chair takes place *via* a chair (C_S) transition state which is 37.2 kJ · mol^{-1} above the crown conformation. The axial-symmetrical twist geometry of the crossed family of (*E*,*E*)-cycloocta-1,4-diene is 5.9 kJ · mol^{-1} less stable than the crown conformation.

Keywords. Medium rings; Stereochemistry; Molecular modelling; Conformational analysis; *ab initio* Calculations.

Introduction

(*Z*,*Z*)-Cycloocta-1,4-diene (**1**) can adopt several conformations, and conformational studies of this molecule have received considerable attention from theoretical [1, 2] and experimental [2] points of view. Although some conformational studies of (*Z*,*Z*)-cycloocta-1,4-diene (**1**) based on dynamic NMR spectroscopy [2] and force-field calculation [1, 2] can be found in the literature, only few

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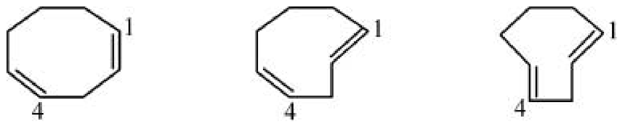


1 **2** **3**

Scheme 1

theoretical studies on the (*E*,*Z*)- and (*E*,*E*)-isomers (Scheme 1) are available, and no example of an isolation of the (*E*,*E*)-isomer **3** has been reported, probably because of instability due to ring strain. Moreover, there is no published study of the relationship between strained structures and strain energies in these compounds.

We here report the results of *ab initio* calculations for structural optimization and conformational interconversion pathways of the strained eight-membered ring dienes **1**–**3** by comparing the geometries (HF/6-31G*) and conformational energies (MP2/6-31G*//HF/6-31G*). The results from these calculations are used in the conformational energies discussions below.

Results and Discussion

(Z,Z)-Cycloocta-1,4-diene (**1**)

(Z,*Z*)-Cycloocta-1,4-diene (**1**) is less stable than (*Z*,*Z*)-cycloocta-1,3-diene, but slightly more stable than (*Z*,*Z*)-cycloocta-1,5-diene [3]. Unlike the 1,3- and 1,5-isomers, this compound has not been investigated in detail. *Dunitz* and *Waser* [4] have pointed out that *Dreiding* molecular models of **1** can exist in a rigid conformation or as a family of flexible conformations. The conformational properties of **1** have been the subject of dynamic NMR studies and force-field calculations [1, 2]. Dynamic NMR spectroscopy has indicated that the compound exists in solution as a mixture of twist-boat (flexible) and boat-chair (rigid) conformations of nearly the same energies. The free-energy barrier for interconversion of these two conformers has been determined to be $33.5\,\mathrm{kJ \cdot mol^{-1}}$.

The results of *ab initio* calculations for structure optimization and conformational interconversion pathways of **1** are shown in Fig. 1 and Tables 1 and 2. Six geometries (three energy minima and three transition states) were found to be important in description of the conformational features of (*Z*,*Z*)-cycloocta-1,4-diene (**1**). The most stable conformation of **1** is the twist-boat form with C_2-symmetry (Fig. 1, Table 1). The calculated energy for the second energy minimum conformation (boat-chair, C_S) is $3.6\,\mathrm{kJ \cdot mol^{-1}}$, which is slightly higher than that ($2.1\,\mathrm{kJ \cdot mol^{-1}}$) determined by dynamic NMR spectroscopy.

The twist-boat or flexible family of conformations of **1** includes the C_2-symmetric twist-boat (**1**-TB) itself and a distorted twist-boat (DTB) which lacks symmetry. The energy barrier separating these conformations is small (Fig. 1, Table 1). The twist-boat conformation changes to its enantiomeric form **1**-TB′ *via* the plane-symmetrical boat-boat (**1**-BB, C_S) geometry as the transition state (Fig. 1). The calculated energy barriers separating the **1**-TB and **1**-TB′ conformations are relatively low (19.1 and $15.8\,\mathrm{kJ \cdot mol^{-1}}$), consistent with the flexibility of

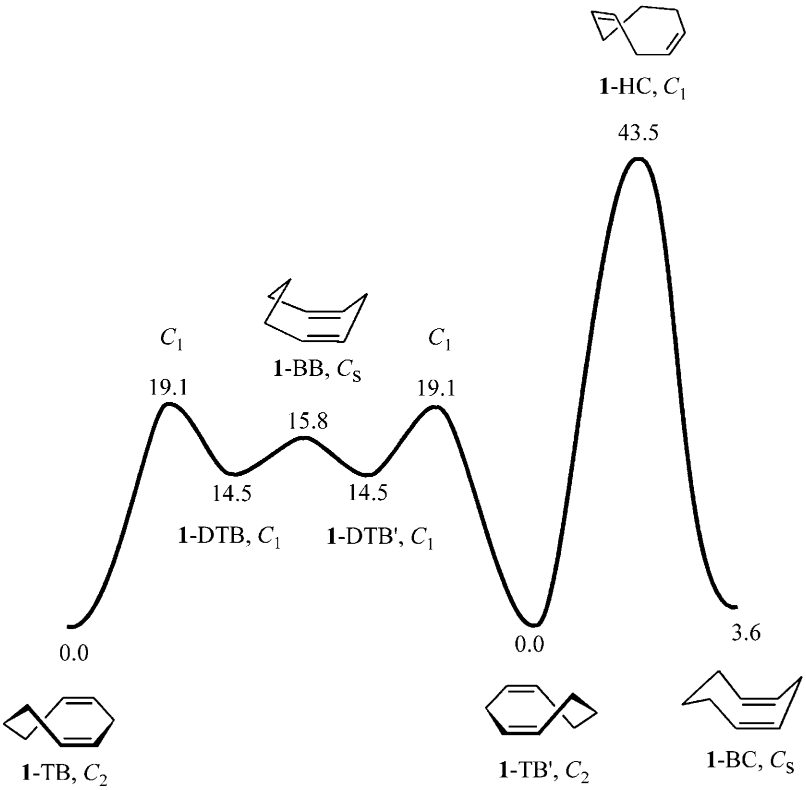


Fig. 1. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ · mol^{-1}) profile for the conformational interconversion of various geometries of (*Z*,*Z*)-cycloocta-1,4-diene (**1**)

Table 1. Calculated total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy (kJ · mol^{-1}), and experimental values (in parentheses) for different geometries of (*Z*,*Z*)-cycloocta-1,4-diene (**1**)

Structure	**1**-TB, C_2	TB ⇌ DTB, C_1	**1**-DTB, C_1	**1**-BB, C_S	**1**-HC, C_1	**1**-BC, C_S
HF/6-31G*//HF/6-31G*	– 309.884752	– 309.877078	– 309.880952	– 309.880904	– 309.869951	– 309.883682
MP2/6-31G*//HF/6-31G*	– 310.909735	– 310.902379	– 310.904289	– 310.903758	– 310.893148	– 310.908484
ZPE/kJ · mol^{-1}	0.193627	0.193549	0.193723	0.193688	0.193614	0.193754
$E_{rel}{}^1$/kJ · mol^{-1}	0.0	19.96	10.20	10.25	38.83	3.11
$E_{rel}{}^2$/kJ · mol^{-1}	0.0 (0.0)	19.13	14.53	15.84	43.52 (33.49)	3.59 (2.1)
$H^o_{298} - H^o_0$/kJ · mol^{-1}	18.71	19.05	21.18	18.83	19.44	20.59
	(0.0)	(0.34)	(2.47)	(0.12)	(0.73)	(1.88)
$G^o_{298} - G^o_0$/kJ · mol^{-1}	– 77.41	– 79.64	– 84.06	– 79.37	– 80.84	– 81.09
	(0.0)	(– 2.23)	(– 6.65)	(– 1.96)	(– 3.43)	(– 3.68)
S^o_{298}/J/mol·°	322.40	331.04	352.98	330.14	336.35	341.00
	(0.0)	(8.64)	(30.58)	(7.74)	(13.95)	(18.60)
$H^o_{168} - H^o_0$/kJ · mol^{-1}	7.31	7.53	8.61	7.36	7.84	8.10
	(0.0)	(0.22)	(1.30)	(0.05)	(0.53)	(0.79)
$G^o_{168} - G^o_0$/kJ · mol^{-1}	– 38.63	– 39.77	– 41.61	– 39.70	– 40.29	– 40.16
	(0.0)	(– 1.14)	(– 2.98)	(– 1.07)	(– 1.66)	(– 1.53)
S^o_{168}/J/mol·°	273.42	281.52	298.96	280.13	286.46	287.29
	(0.0)	(8.10)	(25.54)	(6.71)	(13.04)	(13.87)

[1] Relative energy with respect to the most stable conformation from HF/6-31G*//HF/6-31G* calculations; [2] relative energy with respect to the most stable conformation from MP2/6-31G*//HF/6-31G* calculations

Table 2. Structural parameters for different geometries of (*Z*,*Z*)-cycloocta-1,4-diene (**1**)

Structure	**1**-TB, C_2	TB $\rightleftharpoons$ DTB, C_1	**1**-DTB, C_1	**1**-BB, C_S	**1**-HC, C_1	**1**-BC, C_S
d_{15}/Å	3.42	3.46	3.54	3.55	3.48	3.53
d_{24}/Å	2.65	2.53	2.54	2.54	2.58	2.45
r_{12}/Å	1.322	1.319	1.320	1.320	1.317	1.320
r_{23}/Å	1.516	1.509	1.514	1.517	1.515	1.515
r_{34}/Å	1.516	1.517	1.518	1.517	1.520	1.515
r_{45}/Å	1.322	1.323	1.321	1.320	1.325	1.320
r_{56}/Å	1.509	1.517	1.511	1.509	1.520	1.520
r_{67}/Å	1.538	1.536	1.538	1.534	1.552	1.543
r_{78}/Å	1.538	1.560	1.534	1.534	1.532	1.543
r_{81}/Å	1.509	1.512	1.510	1.509	1.503	1.520
θ_{123}/°	130.6	124.3	127.9	128.2	124.0	124.5
θ_{234}/°	122.0	113.4	113.6	113.7	116.7	110.8
θ_{345}/°	130.6	128.1	128.0	128.2	133.8	124.5
θ_{456}/°	127.5	130.4	131.0	131.4	139.7	126.4
θ_{567}/°	112.8	117.8	119.2	120.8	127.0	116.8
θ_{678}/°	113.1	118.1	115.9	116.5	118.8	116.4
θ_{781}/°	112.8	116.3	119.7	120.8	110.9	116.8
θ_{812}/°	127.5	124.3	130.2	131.4	124.4	126.4
ϕ_{1234}/°	27.1	85.5	79.7	71.4	72.1	82.8
ϕ_{2345}/°	27.1	− 44.8	− 61.7	− 71.4	− 39.9	− 82.8
ϕ_{3456}/°	− 3.7	− 0.3	− 2.0	− 1.7	0.6	− 3.1
ϕ_{4567}/°	− 83.1	− 46.8	− 17.6	2.5	− 9.3	72.5
ϕ_{5678}/°	52.5	81.9	89.2	74.0	− 8.2	− 81.1
ϕ_{6781}/°	52.5	− 1.2	− 57.9	− 74.0	76.4	81.1
ϕ_{7812}/°	− 83.1	− 67.6	− 21.0	− 2.5	− 94.2	− 72.5
ϕ_{8123}/°	− 3.7	0.9	0.4	1.7	− 3.7	3.1

the family including the twist-boat, distorted twist-boat, and boat-boat forms. The transition state for the boat-chair to twist-boat process is the C_S-symmetric half-chair (**1**-HC) which has a relatively high energy, consistent with the rigidity of the boat-chair conformation in *Dreiding* molecular models.

The calculated thermodynamic parameters (H^o, S^o, and G^o) [5, 6] for various geometries of (*Z*,*Z*)-cycloocta-1,4-diene at different temperatures are shown in Table 1. The calculated ΔG^o value of 1.6 kJ · mol^{-1} for **1**-TB and **1**-BC at 168 K is in good agreement with the experimentally determined value of 2.1 kJ · mol^{-1} [2]. The free-energy barrier for the conversion of **1**-TB to **1**-BC ($\Delta G^{\#}=$ 33.49 kJ · mol^{-1}) is lower than that (37.16 kJ · mol^{-1}) calculated at 168 K (see Table 1).

Representative structural parameters for various geometries of **1** are given in Table 2. An important difference between boat-chair and twist-boat conformations concerns the internal angle θ_{234} of the isolated methylene group. This angle (122°) is strongly expanded from its unstrained value (111°) in the twist-boat; in the boat-chair conformation, however, the same angle is slightly compressed. Internal bond angles in medium-ring compounds are usually larger than the unstrained value, a typical angle for saturated eight-membered rings being 114° [7], and it is very unusual for such angles to have a value less than 111°. The internal angles of the olefinic carbons in the boat-chair are almost normal, whereas those of the twist-boat and distorted twist-boat are quite expanded.

(E,Z)-Cycloocta-1,4-diene (**2**)

Deoxygenation of the monoepoxide of (*Z*,*Z*)-cycloocta-1,4-diene (**1**) with lithium diphenylphosphide followed by methyl iodide proceeds with overall inversion of stereochemistry and affords (*E*,*Z*)-cycloocta-1,4-diene (**2**) in 40% yield [8]. Whereas much work has been dedicated to the study of the structure and properties of **1**, much less effort has been devoted to the (*E*,*Z*)-isomer **2**. Altogether four geometries were found to be important for description of the conformational features of **2**. Two of these geometries correspond to energy minima and two to one-dimensional energy maxima as shown in Fig. 2 and Table 3.

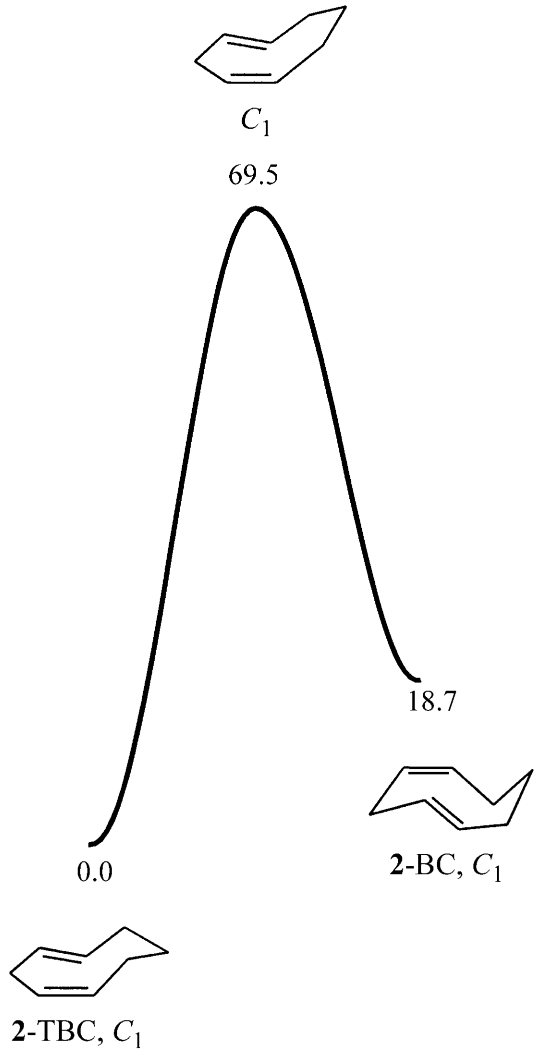


Fig. 2. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ · mol^{-1}) profile for the conformational interconversion of twist-boat-chair and boat-chair geometries of (*E*,*Z*)-cycloocta-1,4-diene (**2**)

Table 3. Calculated total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy ($\mathrm{kJ \cdot mol^{-1}}$), and structural parameters for various conformations of (*E*,*Z*)-cycloocta-1,4-diene (**2**)

Structure	**2**-TBC, C_1	TBC $\rightleftharpoons$ BC, C_1	**2**-BC, C_1	Swiveling
HF/6-31G*//HF/6-31G*	– 309.860034	– 309.835171	– 309.853396	– 309.792579
MP2/6-31G*//HF/6-31G*	– 310.890490	– 310.863780	– 310.883202	– 2310.85118
$ZPE/\mathrm{kJ \cdot mol^{-1}}$	0.193476	0.193221	0.193289	0.193885
$E_{\mathrm{rel}}{}^{1}/\mathrm{kJ \cdot mol^{-1}}$	0.0	64.66	16.97	178.08
$E_{\mathrm{rel}}{}^{2}/\mathrm{kJ \cdot mol^{-1}}$	0.0	69.51	18.68	172.61
$H^{\circ}_{298} - H^{\circ}_{0}/\mathrm{kJ \cdot mol^{-1}}$	20.38	19.61	21.05	19.30
	(0.0)	(– 0.77)	(0.67)	(– 1.08)
$G^{\circ}_{298} - G^{\circ}_{0}/\mathrm{kJ \cdot mol^{-1}}$	– 80.71	– 81.34	– 82.13	– 80.29
	(0.0)	(– 0.63)	(– 1.42)	(0.42)
$S^{\circ}_{298}/\mathrm{J/mol \cdot ^{\circ}}$	339.05	338.59	346.07	334.03
	(0.0)	(– 0.46)	(7.02)	(– 5.02)
$d_{15}/\mathrm{\AA}$	3.08	3.15	3.16	3.76
$d_{24}/\mathrm{\AA}$	2.45	2.38	2.42	2.36
$r_{12}/\mathrm{\AA}$	1.318	1.314	1.315	1.314
$r_{23}/\mathrm{\AA}$	1.501	1.490	1.503	1.496
$r_{34}/\mathrm{\AA}$	1.522	1.521	1.522	1.538
$r_{45}/\mathrm{\AA}$	1.330	1.332	1.332	1.341
$r_{56}/\mathrm{\AA}$	1.534	1.544	1.540	1.569
$r_{67}/\mathrm{\AA}$	1.552	1.582	1.554	1.586
$r_{78}/\mathrm{\AA}$	1.552	1.548	1.551	1.573
$r_{81}/\mathrm{\AA}$	1.494	1.489	1.495	1.537
$\theta_{123}/^{\circ}$	119.5	121.5	121.1	157.2
$\theta_{234}/^{\circ}$	107.9	104.6	106.2	101.9
$\theta_{345}/^{\circ}$	130.1	131.5	131.1	129.2
$\theta_{456}/^{\circ}$	133.6	142.6	136.7	136.5
$\theta_{567}/^{\circ}$	119.8	134.8	121.9	124.3
$\theta_{678}/^{\circ}$	114.2	123.7	115.1	122.4
$\theta_{781}/^{\circ}$	104.3	106.4	105.6	114.7
$\theta_{812}/^{\circ}$	122.0	119.6	120.7	110.3
$\phi_{1234}/^{\circ}$	66.8	82.9	80.6	176.0
$\phi_{2345}/^{\circ}$	5.0	– 27.7	– 26.7	6.6
$\phi_{3456}/^{\circ}$	8.1	– 11.3	– 5.3	6.0
$\phi_{4567}/^{\circ}$	– 80.5	33.0	59.5	– 52.6
$\phi_{5678}/^{\circ}$	86.7	24.6	– 90.3	87.0
$\phi_{6781}/^{\circ}$	– 52.7	– 32.5	38.3	– 60.0
$\phi_{7812}/^{\circ}$	83.7	94.3	59.4	18.8
$\phi_{8123}/^{\circ}$	– 137.1	– 149.2	– 137.4	– 178.3

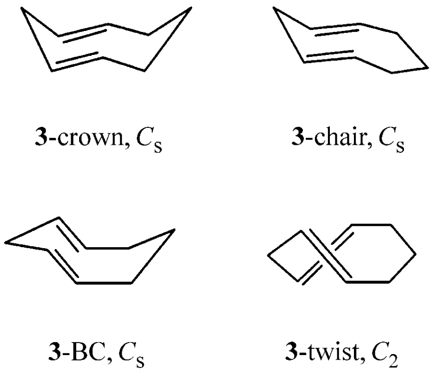
[1] Relative energy with respect to the most stable conformation from HF/6-31G*//HF/6-31G* calculations; [2] relative energy with respect to the most stable conformation from MP2/6-31G*//HF/6-31G* calculations

The twist-boat-chair (**2**-TBC) conformation is by 18.7 $\mathrm{kJ \cdot mol^{-1}}$ more stable than the boat-chair (**2**-BC) form. Thus, compound **2** is expected to be conformationally homogeneous at ambient temperature. As shown in Table 3, both forms

Table 4. Calculated total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy ($\mathrm{kJ\cdot mol^{-1}}$), and structural parameters for various conformations of (*E*,*E*)-cycloocta-1,4-diene (**3**)

Structure	**3**-crown, C_S	**3**-chair, C_S	**3**-BC, C_S	**3**-twist, C_2
HF/6-31G*//HF/6-31G*	– 309.809996	– 309.796251	– 309.802586	– 309.800620
MP2/6-31G*//HF/6-31G*	– 310.850055	– 310.835590	– 310.843528	– 310.839976
$ZPE/\mathrm{kJ\cdot mol^{-1}}$	0.192724	0.192395	0.192462	0.191977
$\mathrm{E_{rel}}^1/\mathrm{kJ\cdot mol^{-1}}$	0.0	35.30	18.83	5.46
$\mathrm{E_{rel}}^2/\mathrm{kJ\cdot mol^{-1}}$	0.0	37.19	16.51	5.90
$H^{o}_{298} - \mathrm{H}^{o}_{0}/\mathrm{kJ\cdot mol^{-1}}$	20.31	19.48	20.84	19.66
	(0.0)	(– 0.83)	(0.53)	(– 0.65)
$G^{o}_{298} - G^{o}_{0}/\mathrm{kJ\cdot mol^{-1}}$	– 80.19	– 80.02	– 81.00	– 78.35
	(0.0)	(0.17)	(– 0.81)	(1.84)
$S^{o}_{298}/\mathrm{J/mol}\cdot^{\circ}$	337.05	333.74	341.49	330.11
	(0.0)	(– 3.31)	(4.44)	(– 6.94)
$d_{15}/\text{Å}$	2.38	2.75	2.76	2.85
$d_{24}/\text{Å}$	2.24	2.27	2.29	2.34
$r_{12}/\text{Å}$	1.322	1.321	1.322	1.323
$r_{23}/\text{Å}$	1.533	1.533	1.536	1.537
$r_{34}/\text{Å}$	1.533	1.533	1.536	1.537
$r_{45}/\text{Å}$	1.322	1.321	1.322	1.323
$r_{56}/\text{Å}$	1.510	1.504	1.515	1.505
$r_{67}/\text{Å}$	1.572	1.604	1.574	1.591
$r_{78}/\text{Å}$	1.572	1.604	1.574	1.591
$r_{81}/\text{Å}$	1.510	1.504	1.515	1.505
$\theta_{123}/^{\circ}$	120.2	118.8	118.6	120.5
$\theta_{234}/^{\circ}$	94.1	95.6	96.1	99.2
$\theta_{345}/^{\circ}$	120.2	118.8	118.6	120.5
$\theta_{456}/^{\circ}$	122.4	123.6	124.1	121.6
$\theta_{567}/^{\circ}$	108.8	113.7	110.4	112.2
$\theta_{678}/^{\circ}$	122.2	127.5	123.3	125.0
$\theta_{781}/^{\circ}$	108.8	113.7	110.4	112.2
$\theta_{812}/^{\circ}$	122.4	123.6	124.1	121.6
$\phi_{1234}/^{\circ}$	75.7	72.5	72.4	45.9
$\phi_{2345}/^{\circ}$	– 75.7	– 72.5	– 72.4	45.9
$\phi_{3456}/^{\circ}$	122.5	126.7	123.7	– 127.1
$\phi_{4567}/^{\circ}$	– 97.4	– 77.9	– 58.0	93.3
$\phi_{5678}/^{\circ}$	56.0	– 3.1	– 45.4	– 22.8
$\phi_{6781}/^{\circ}$	– 56.0	3.1	45.4	– 22.8
$\phi_{7812}/^{\circ}$	97.4	77.9	58.0	93.3
$\phi_{8123}/^{\circ}$	– 122.5	– 126.7	– 123.7	– 127.1

[1] Relative energy with respect to the most stable conformation from HF/6-31G*//HF/6-31G* calculations; [2] relative energy with respect to the most stable conformation from MP2/6-31G*//HF/6-31G* calculations


3-crown, C_s **3**-chair, C_s

3-BC, C_s **3**-twist, C_2

Scheme 2

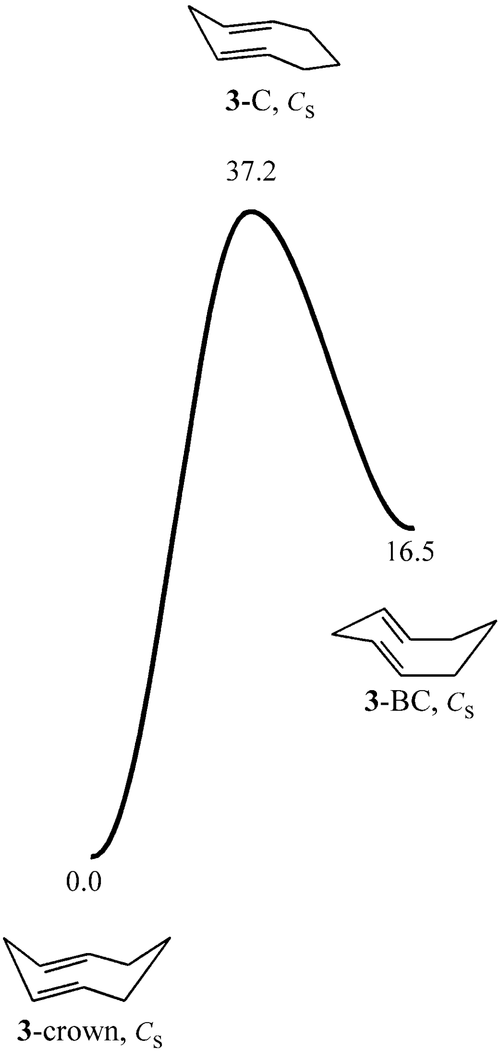


Fig. 3. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ · mol^{-1}) profile for the conformational interconversion of crown and boat-chair geometries of (*E*,*E*)-cycloocta-1,4-diene (**3**)

have a slightly distorted *cis*-double bond with a ϕ_{3456} angle of 5–8° and a strongly twisted *trans*-double bond with a ϕ_{8123} angle of 137°. The transition state linking **2**-TBC and **2**-BC conformations is calculated to be by 69.5 kJ · mol^{-1} less stable than the **2**-TBC form. A second (high-energy) process involves degenerate interconversion of the **2**-TBC conformation with its mirror-image geometry. This process involves swiveling [9] of the *trans*-double bond through the unsaturated bridge, which requires 172.6 kJ · mol^{-1}. If both processes considered are fast, the time-averaged symmetry of the twist-boat-chair conformation becomes C_S, which is the maximum symmetry allowed by the chemical structure of (*E*,*Z*)-cycloocta-1,4-diene (**2**).

(E,E)-Cycloocta-1,4-diene (**3**)

Two families of conformations, the crossed and parallel, are possible for **3** (Scheme 2). The most stable conformation of the parallel family is the crown (**3**-crown, C_S) conformer, which was calculated to be by 5.9 kJ · mol^{-1} more stable than the boat geometry (**3**-twist, C_2) of the crossed family (Table 4). As shown in Fig. 3 and Table 4, the crown conformation of **3** is by 16.5 kJ · mol^{-1} more stable than the C_S-symmetric boat-chair form. Interconversion of the two energy-minimum geometries of the parallel family of **3** takes place *via* a C_S-symmetric chair transition state which is by 37.2 kJ · mol^{-1} less stable than the crown conformation. Interconversion of the parallel and crossed families of **3** formally can take place by swiveling of one of the double bonds through the unsaturated bridge [9]. However, the energy required for this process is higher than the π-bond dissociation energy.

The thermodynamic parameters for important geometries of the parallel and crossed families of (*E*,*E*)-cycloocta-1,4-diene at 0 K and 298 K are shown in Table 4. The crown conformation of the parallel family is calculated to be the most favoured geometry at these temperatures.

Conclusions

HF/6-31G* calculations provide a picture of the conformations of (*Z*,*Z*)-, (*E*,*Z*)-, and (*E*,*E*)-cycloocta-1,4-dienes (**1**–**3**) from both structural and energetic points of view. The agreement between the HF/6-31G* results obtained for **1** and the dynamic NMR spectroscopic results [2] is fairly good. Compound **2** is expected to be conformationally homogeneous at room temperature. Compound **3**, however, is predicted to exist as a mixture of parallel and crossed families.

Methods

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 [10] program. Geometries for all structures were fully optimized by means of analytical energy gradients using the *Berny* optimizer with no geometrical constraints [11]. The restricted *Hartree-Fock* calculations with the split-valence 6-31G* basis set which includes a set of d-type polarization functions on all non-hydrogen atoms were used in these calculations [12]. Single point energy calculations at the MP2/6-31G*//HF/6-31G* level were used to evaluate the electron correlation effect in the energies and the order of stability of conformers.

Vibrational frequencies were calculated at the 6-31G* level for all minimum energies and transition states which were confirmed to have zero and one imaginary frequency. The frequencies were scaled by a factor of 0.91 [13] and used to compute the zero-point vibrational energies.

Theoretical calculations are not expected, in principle, to reproduce the experimental values quantitatively [14]. Nevertheless, it is possible to carry out *ab initio* calculations at the *Hartree-Fock* level from which many properties and structural features can be obtained with an accuracy that is competitive with experiment [15, 16]. Since the theoretical results are free from intermolecular interferences, they are a valuable tool for a systematic study of conformational effects in simple organic molecules.

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